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(54) Title: COLOR-STABILIZATION SYSTEM IN LIQUID DETERGENT COMPOSITIONS

(57) Abstract

Liquid detergent compositions are described which comprise conventional detergency ingredients and color-stabilizing compounds yielding various sulfite ions in the finished product.

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COLOR-STABILIZATION SYSTEM IN LIQUID DETERGENT COMPOSITIONS

Technical field

The present invention relates to liquid detergent compositions. The compositions according to the present invention are stabilized against color alteration.

Background of the invention

Liquid detergent compositions are well known in the art. It is desirable that such compositions should have an attractive color as the compositions aesthetics is a key element in terms of consumer acceptance. A broad palette of dyes is available to the detergent formulator in order to address this need.

As an alternative, some compositions can be marketed without dyes, when the color of the product without dyes is sufficiently attractive.

However, it has been observed that in certain liquid detergent formulations, the color of the fresh product would not remain unchanged through prolonged periods. This represents a problem for the detergent manufacturer as detergents should be capable of withstanding prolonged periods of storage without undergoing significant alteration in any respect, including product aesthetics.

The reasons for this color alteration have not been precisely identified, but it is believed that such ingredients as alkanolamines are to some extent responsible for this phenomenon. Perfumes also appear to play a role, quite undefined because of the complex nature of perfumes. Thus, the extent of the color alteration phenomenon throughout time varies from one composition to the other.

It has been observed that this color alteration phenomenon occurs in detergent compositions, irrespective of the presence of a dye, i.e. it is the color of the "base" without the dye which is altered. Unfortunately, the presence of a dye does not always suffice to mask the color alteration phenomenon.

The above problem is more accute in "modern" liquid detergents as these detergents tend to be formulated as so-called concentrated liquid detergents wherein the interaction between the different ingredients and therefore the color alteration is favored. Also, these liquid concentrated detergents often encompass the use of alkanolamines which, as mentioned hereinabove, are to some extent responsible for the color alteration phenomenon.

It is thus an object of the present invention to formulate liquid detergent compositions which are stabilized against color alteration throughout prolonged periods.

In response to this object, the present invention proposes to formulate liquid detergent compositions which comprise low levels of materials yielding various sulfite ions in the detergent composition, as color-stabilizing compounds.

An advantage of the present invention is that it offers a color stabilization system which is efficient in all products where color alteration occurs, with or without dye. It is another advantage of the present invention that

it proposes the use of simple chemicals, which are commercially available and relatively in xpensive.

Summary of the invention

The compositions according to the present invention are liquid detergent compositions comprising conventional detergency ingredients, characterized in that they further comprise from 0.001% to 10% by weight of the total composition of a color-stabilizing compound selected from sulfite, hydrogenosulfite or pyrosulfite salts, sulfur dioxide, sulfurous acid, alpha-hydroxy alkyl sulfonic acids, mercaptoethanol, sodium mercaptoacetate, 2-aminoethanethiol, cystein, polycycstein, glutathione and formamidine sulfinic acid, or mixtures thereof.

Detailed description of the invention

The liquid detergent compositions according to the present invention comprise conventional detergency ingredients and the color stabilization system.

As the color stabilization system, the detergent compositions according to the present invention comprise from 0.001% to 10% by weight of the total composition of a compound selected from sulfite (SO_3^{2-}), hydrogenosulfite (HSO_3^-) or pyrosulfite salts ($S_2O_5^{2-}$), sulfur dioxide, sulfurous acid, alpha-hydroxy alkyl sulfonic acids, mercaptoethanol, sodium mercaptoacetate, 2-aminoethanetiol, cystein, polycystein, glutathione and formamidine sulfinic acid, or mixtures thereof. Suitable sulfite, hydrogenosulfite and pyrosulfite salts include metal salts, ammomium salts and alkanolammonium salts. Preferred salts for use herein are sodium, potassium, calcium,

alkanolammonium and ammonium salts. These compounds are commonly used as food preservatives and are therefore commercially available. Hydrogenosulfite, sulfur dioxid and sulfurous acid solutions are also commercially available.

The preferred color-stabilizing compound according to the present invention is sodium pyrosulfite.

Without wanting to be bound by theory, it is believed that it is hydrogenosulfite ions which are mainly responsible for the color-stabilizing effect observed. However, any of the compounds described hereinabove can be added to the detergent composition as said compounds are all believed to yield hydrogenosulfite ions in the finished product. Alpha-hydroxyalkyl sulfonic acids are therefore also suitable for use in the compositions according to the invention as they yield hydrogenosulfite ions in the finished product. Alpha-hydroxy alkyl sulfonic acids can be prepared by reacting aldehydes or ketones with Na bisulfite, as described for instance in J. March, Advanced Organic Chemistry, Mc Graw-Hill, 1977, page 816. The alkyl chain lenght and configuration of the alpha-hydroxy alkyl sulfonic acid is not critical herein. Preferred alkyl chains are C_1 to C_{15} aliphatic chains.

Preferably, the compositions according to the present invention comprise from 0.005% to 1% by weight of the total composition of said color-stabilizing compounds or mixtures thereof, most preferably from 0.01% to 0.1%.

The rest of the liquid detergent composition according to the present invention is made of conventional detergency ingredients, i.e. water, surfactants, builders and others.

The liquid detergent compositions herein comprises from 5% to 60% by weight of the total liquid detergent composition,

preferably from 20% by weight to 40% by weight of an organic surface-active agent selected from nonionic, anionic, cationic and zwitterionic surface-active agents and mixtures thereof.

Suitable anionic surface-active salts are selected from the group of sulfonates and sulfates. The like anionic surfactants are well-known in the detergent art and have found wide application in commercial detergents. Preferred anionic water-soluble sulfonate or sulfate salts have in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms. Examples of such preferred anionic surfactant salts are the reaction products obtained by sulfating C_8-C_{18} fatty alcohols derived from e.g. tallow oil, palm oil, palm kernel oil and coconut oil; alkylbenzene sulfonates wherein the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkylglyceryl ether sulfonates; ether sulfates of fatty alcohols derived from tallow and coconut oils; coconut fatty acid monoglyceride sulfates and sulfonates; and water-soluble salts of paraffin sulfonates having from about 8 to about 22 carbon atoms in the alkyl chain. Sulfonated olefin surfactants as more fully described in e.g. U.S. Patent Specification 3,332,880 can also be used. The neutralizing cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium or alkanolammonium.

A suitable anionic synthetic surfactant component herein is represented by the water-soluble salts of an alkylbenzene sulfonic acid, preferably sodium alkylbenzene sulfonates, preferably sodium alkylbenzene sulfonates having from about 10 to 13 carbon atoms in the alkyl group. Another preferred anionic surfactant component herein is sodium alkyl sulfates having from about 10 to 15 carbon atoms in the alkyl group.

The nonionic surfactants suitable for use herein include those produced by condensing ethylene oxide with a hydrocarbon having a reactive hydrogen atom, e.g., a hydroxyl, carboxyl, or amido group, in the presence of an acidic or basic catalyst, and include compounds having the general formula $RA(CH_2CH_2O)_nH$ wherein R represents the hydrophobic moiety, A represents the group carrying the reactive hydrogen atom and n represents the average number of ethylene oxide moieties. R typically contains from about 8 to 22 carbon atoms They can also be formed by the condensation of propylene oxide with a lower molecular weight compound. n usually varies from about 2 to about 24.

A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from about 4 to 10 moles of ethylene oxide per mole or fatty alcohol. Suitable species of this class of ethoxylates include : the condensation product of C_{12}-C_{15} oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of alcohol; the condensation product or narrow cut C_{14}-C_{15} oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of fatty(oxo)alcohol; the condensation product of a narrow cut C_{12}-C_{13} fatty(oxo)alcohol and 6,5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a C_{10}-C_{14} coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 4 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching. A degree of branching in the range from 15% to 50% (weight%) is frequently found in commercial oxo alcohols.

Suitable cationic surfactants include quaternary ammonium compounds of the formula $R_1R_2R_3R_4N^+$ where R_1,R_2 and R_3 are

methyl groups, and R_4 is a C_{12-15} alkyl group, or wh re R_1 is an ethyl or hydroxy ethyl group, R_2 and R_3 are methyl groups and R_4 is a C_{12-15} alkyl group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds in which the aliphatic moiety can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 24 carbon atoms and another substituent contains, at least, an anionic water-solubilizing group. Particularly preferred zwitterionic materials are the ethoxylated ammonium sulfonates and sulfates disclosed in U.S. Patents 3,925,262, Laughlin et al., issued December 9, 1975 and 3,929,678, Laughlin et al., issued December 30, 1975.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl or hydroxy alkyl moiety of from about 8 to about 28 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups, containing from 1 to about 3 carbon atoms which can optionally be joined into ring structures.

Also suitable are Poly hydroxy fatty acid amide surfactants of the formula $R^2-\overset{\overset{O}{\|}}{C}-\overset{\overset{R^1}{|}}{N}-Z$, wherein R^1 is H, C_{1-4}hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R_2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R_1 is methyl, R_2 is a straight C_{11-15} alkyl or alkenyl chain or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R_CH(COOH)CH_2(COOH) wherein R is C_{10-20} alkyl or alkenyl, preferably C_{12-16}, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substitutents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium. ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071

Suitable fatty acid builders for use herein are saturated or unsaturated C_{10-18} fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

A preferred builder system for use herein consists of a mixture of citric acid, fatty acids and succinic acid derivatives described herein above. The builder system

according to the present invention preferably represents from 5% to 35% by weight of the total composition.

The compositions according to the invention preferably comprise enzymes. Suitable enzymes for use herein are protease, lipases, cellulases and amylases and mixtures thereof. The compositions according to the present invention may also comprise an enzyme stabilizing system. Any conventional enzyme stabilizing system is suitable for use herein, and preferred enzyme stabilizing systems are based on boric acid or derivatives thereof, 1,2-propanediol, carboxylic acids, and mixtures thereof.

The compositions herein can contain a series of further, optional ingredients. Examples of the like additives include solvents, alkanolamines, pH adjusting agents, suds regulants, opacifiers, agents to improve the machine compatibility in relation to enamel-coated surfaces, perfumes, dyes, bactericides, brighteners, soil release agents, softening agents and the like. Some of these ingredients are believed to have an effect on the color alteration problem underlying the present invention, particularly perfumes and alkanolamines.

The compositions according to the present invention can be formulated as conventional liquid detergent compositions or, as an alternative as so-called "concentrated" liquid detergent compositions, i.e. liquid detergent compositions comprising less than 30% by weight of water.

Examples

The following compositions are made which illustrate th present invention. Compositions I-IV and VIII are concentrated liquid detergent compositions.

	I %	II %	III %	IV %
Alkyl benzene sulfonic acid	15	13	18	16
Na Coconut Alkyl sulfate	4	5	2	-
C13-15 alcohol 7 ethoxylated	13.4	15	13.5	13
Coconut alkyl sulfate 3 ethoxylate	-	-	-	3
Coconut N-methlyl glucosamide	-	-	-	-
Coconut fatty acid	11	4	8.5	7.5
Dodecenyl succinic acid	6	8	7	6
Citric acid	5.5	5.9	6	5
Tartrate momo succinate	-	-	-	
Diethylene triamine pentamethylene phosphonic acid	0.9	0.9	1.1	-
Ethanol	1.5	1.5	3	-
Propandiol	9.5	8.8	9	6
Monoethanolamine	8	12.5	14	1
Triethanolamine	-	-	-	15
Sodium metaborate	2	2	2	-
Sodium pyrosulfite	0.05	-	-	0.01
Sodium sulfite	-	0.075	-	-
Potassium bisulfite	-	-	0.1	-
Sulfur dioxide	-	-	-	
Enzymes	0.8	0.8	1.2	0.8
Perfume	0.5	0.5	0.6	0.5
Dyes	25ppm	-	25ppm	25ppm
Sodium (potassium)hydroxide:to pH	7.5	7.5	7.5	7.5
Water and minors	-------	to 100	-------	-------

	V	VI	VII	VIII	IX
	%	%	%	%	%
Alkyl benzene sulfonic acid	10.4	10.2	12	-	-
Na Coconut Alkyl sulfate	2.5	2.8	2	-	-
C13-15 alcohol 7 ethoxylated	9.2	11.6	8.5	5	3
Coconut alkylsulfate 3 ethoxylated	-	-	-	20	13
Coconut N-methlyl glucosamide	-	-	-	11	6
Coconut fatty acid	-	12	-	8	5
Dodecenyl succinic acid	6	-	10.5	3	-
Citric acid	8	-	3.5	5	2
Tartrate momo succinate	-	-	-	-	3
Diethylene triamine pentamethylene phosphonic acid	0.7	0.7	0.5	0.5	0.5
Ethanol	4	7	4	4	4
Propandiol	4.5	1.5	2	6	3
Monoethanolamine	-	-	-	5	2
Triethanolamine	-	6.5	-	-	2
Sodium Metaborate	1	-	2	2	1
Sodium pyrosulfite	-	0.02	-	0.05	-
Sodium sulfite	-	-	0.01	-	-
Potassium bisulfite	-	-	-	-	0.03
Sulfur dioxide	0.01	-	-	-	-
Enzymes	0.8	0.5	0.5	1	0.7
Perfume	0.5	0.4	0.3	0.5	0.3
Dyes	25ppm	10ppm	15ppm	-	25ppm
Sodium (potassium)hydroxide:to pH	7.5	7.5	7.5	7.5	7.5
Water and minors	----	----	to 100	----	----

Experimental Part

The following comp sition was made:

	%
Alkyl benzene sulfonic acid	15.2
MEA Coconut Alkyl sulfate	4
C13-15 alcohol 7 ethoxylated	13.4
Coconut alkyl sulfate 3 ethoxylate	-
Coconut N-methyl glucosamide	-
Coconut fatty acid	8.5
Dodecenyl sussinic acid	6.9
Citric acid	5.9
Tartrate mono succinate	-
Diethylene triamine pentamethylene phosphonic acid	0.9
Ethanol	1.5
Propandiol	8.8
Sodium hydroxide	-
Potassium hydroxide	0.25
Monoethanolamine	12.5
Triethanolamine	-
MEA Metaborate	2
Enzymes	0.8
Perfume	0.5
Opacifier	1.2
Acid blue 80	25ppm
Acid blue 7	14ppm
Water and minors	to 100

The color of this composition was defined immediately after it was made by measuring its Hunter parameters (L,a and b values). Therafter, one sample (sample 1) of this composition was supplemented with 1000 ppm sodium pyrosulphite and stored for two weeks at room temperature.

Another sample (sample 2= Ref) of the composition above was also stored in the same conditions without any color stabilizer being added. After two weeks, the Hunter parameters of the two samples were measured. Results were as follows:

	Fresh	After two weeks storage	
		sample 1	sample 2 = ref
L	37	37	36
a	-9	-9	-12
b	-22	-23	-12
Appearance	Blue	Blue	Green

Conclusion:

After two weeks storage at room temperature, the color of the sample without any color-stabilizing system according to the present invention already differs substantially from the color of the fresh product, whereas the color of the sample comprising a color stabilizing system according to the present invention is virtually unchanged; a difference, if any, is certainly not visually detectable.

CLAIMS

1. A liquid detergent composition comprising conventional detergency ingredients, characterized in that it comprises a color-stabilizing compound selected from sulfite, hydrogenosulfite or pyrosulfite salts, sulfur dioxide, sulfurous acid, alpha-hydroxy alkyl sulfonic acids, mercaptoethanol, sodium mercaptoacetate, 2-aminoethanetiol, cystein, polycystein, gluthatione and formamidine sulfinic acid, or mixtures thereof.

2. A composition according to claim 1, which comprises from 0.001% to 10% by weight of the total composition of said color-stabilizing compound or mixtures thereof.

3. A composition according to claim 2 which comprises from 0.005% to 1% by weight of the total composition of said color-stabilizing compound or mixtures thereof.

4. A composition according to claim 3, which comprises from 0.01% to 0.1% by weight of the total composition of said color-stabilizing compound or mixtures thereof.

5. A composition according to the preceding claims wherein said salts of sulfite, hydrogenosulfite and pyrosulfite are metal salts, ammonium salts and alkanolammonium salts.

6. A composition according to the preceding claims, characterized in that said color-stabilizing compound is sodium pyrosulfite.

7. A composition according to the preceding claims which comprises an alkanolamine.

8. A composition according to the preceding claims wherein said conventional ingredients include surfactants and detergency builders.

9. A composition according to the preceding claims which contains less than 30% by weight of the total composition of water.

INTERNATIONAL SEARCH REPORT

PCT/US92/09387

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C11D 3/04, 3/34, 7/08, 7/10
US CL :252/151, 252/545, 252/549, 252, DIG. 4, 252/DIG. 14
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS - Sodium pyrosulfite, color, detergent#

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,014,807 (Werner et al) 29 March 1979, See column 2, lines 40-44 & column 3, lines 7-11.	1-4
X X	US, A, 4,077,911 (Okumura et al) 07 March 1978, See column 1, line 68 - column 2, line 7 & column 6, lines 27-35.	1-4 1-4
Y	US, A, 4,741,854 (Krupa et al) 03 May 1988, See column 4, lines 60-65.	1-4
X Y	US, A, 4,364,837 (Pader) 21 December 1982, See column 13, 61-62 & column 14, 34-49.	1-4 1-4

☐ *Further documents are listed in the continuation of Box C.* ☐ *See patent family annex.*

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 30 DECEMBER 1992	Date of mailing of the international search report 25 JAN 1993
Name and mailing address of the ISA/ Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer DAVID A. ZARNEKE Telephone No. (703) 308-2521

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/09387

Box I Observations where certain claims were found unsearchable (Continuation f item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-9
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any addtional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.